

PATENT ABSTRACTS OF JAPAN

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(54) WHITE POLYLACTIC ACID FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a low-density white film having no problem at dumping, excellent whiteness and cushioning properties.

SOLUTION: This white polylactic acid film is characterized in that the film comprises a polylactic acid and a resin incompatible with the polylactic acid as main constitutive components and has fine voids inside.

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CLAIMS

[Claim(s)]

[Claim 1]A white polylactic acid film containing a detailed cave in an inside which makes a main constituent polylactic acid and resin immiscible to this.

[Claim 2]this -- the white polylactic acid film according to claim 1, wherein immiscible resin is thermoplastics.

[Claim 3]The white polylactic acid film according to claim 2, wherein this thermoplastics is polyester which consists of an acid component and a glycol component.

[Claim 4]The white polylactic acid film according to claim 3 to which this polyester is characterized by being terephthalic acid and polyester whose main glycol component is ethylene glycol by main acid component.

[Claim 5]The white polylactic acid film according to claim 2, wherein this thermoplastics is polyolefine.

[Claim 6]The white polylactic acid film according to claim 5, wherein this polyolefine is polypropylene.

[Claim 7]The white polylactic acid film according to any one of claims 1 to 6, wherein this white polylactic acid film is what has the apparent density of 0.30 - 1.24 g/cm³.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]About a white polylactic acid film, in more detail, this invention has a void inside, is excellent in white nature and cushioning properties, and relates to the white polylactic acid film which maintains the feature of polylactic acid and is not accumulated under after-abandonment natural environment.

[0002]

[Description of the Prior Art]After carrying out mixed film production of polyethylene terephthalate resin and the resin immiscible to this conventionally as a white film which contains a detailed cave inside, the method of making the detailed cave which extended to 2 shaft orientations and used immiscible resin as the core form is known. As immiscible resin, polyolefin resin is used in many cases, and polypropylene, a polymethylpentene, or polystyrene is known. And such a white film is used for a television film, a label, etc. [0003]However, such a white film currently used from the former will remain in the ground or underground semipermanently, when it is neglected after use or flasking processing is carried out into the ground, since it did not decompose under natural environment, or catabolic rate is very low. When sea dumping is carried out, a scene is spoiled or the living environment of a marine organism is destroyed. When incineration processing is carried out, waste treatment serves as a social problem with expansion of consumption of promoting degradation of an incinerator etc. with the high combustion heat.

[0004]Although the white film which consists of polylactic acid which has biodegradability on the other hand is also proposed (JP,11-268404,A), since the inorganic filler is used, If a cave cannot become large easily, tends to enlarge and enlarges the particle diameter of an inorganic filler, When ductility fell, and it tried to increase the number of the cave and the addition of the inorganic filler was increased, there was a problem that it was difficult to be compatible in white nature -- density will go up -- cushioning properties, and low density-ization.

[0005]

[Problem(s) to be Solved by the Invention]This invention cancels the fault of this conventional technology, does not have a problem at the time of abandonment, is excellent in white nature or cushioning properties, and uses the white film of low density as an offer plug.

[0006]

[Means for Solving the Problem]The following means are used for this invention in order to solve this

technical problem. That is, a white polylactic acid film of this invention contains a detailed cave in an inside which makes a main constituent polylactic acid and resin immiscible to this.

[0007]

[Embodiment of the Invention]When it sees as a film which blends specific resin with polylactic acid and has a cave when this invention does not have said technical problem, i.e., the problem at the time of abandonment, it excels in white nature or cushioning properties and the white film of low density is examined wholeheartedly, it studies solving this technical problem at once.

[0008]If the polylactic acid in this invention is the copolymers of polylactic acid or lactic acid, and other hydroxycarboxylic acid, or these mixtures and is a range which does not check the purpose of this invention, it is the purpose of adjusting handling nature, processability, and physical properties, Additive agents, such as a plasticizer, lubricant, a thermostabilizer, coloration inhibitor, an ultraviolet ray absorbent, light stabilizer, and an antioxidant, may be made to contain.

[0009]As lactic acid, L-lactic acid and D-lactic acid are mentioned and glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyrate, 4-hydroxyvaleric acid, 5-hydroxyvaleric acid, and 6-hydroxycaproic acid are mentioned as other hydroxycarboxylic acid.

[0010]In this invention, polylactic acid and immiscible resin are resin in which phase separation is shown in the state where it sheet-ized, after kneading, are thermoplastics preferably, and are polyester or polyolefin which consists of an acid component and a glycol component still more preferably.

[0011]As polyester which consists of an acid component and a glycol component, the polyester which makes a main constituent aromatic dicarboxylic acid, aliphatic dicarboxylic acid or alicycle fellows dicarboxylic acid, and glycol can be mentioned. As this aromatic dicarboxylic acid component, compare and **, terephthalic acid, isophthalic acid, Phthalic acid, 1, 4-naphthalene dicarboxylic acid, 1, 5-naphthalene dicarboxylic acid, Terephthalic acid, isophthalic acid, 2, and 6-naphthalene dicarboxylic acid can be mentioned preferably also in 2,6-naphthalene dicarboxylic acid, 4,4'-diphenyldicarboxylic acid, 4,4'-diphenyl ether dicarboxylic acid, and 4,4'-diphenylsulfone dicarboxylic acid. As an aliphatic dicarboxylic acid component, adipic acid, suberic acid, sebacic acid, dodecane dione acid, etc. can be mentioned, for example. As an alicycle fellows dicarboxylic acid component, 1 and 4-cyclohexanedicarboxylic acid etc. can be mentioned, for example. Only one sort of these acid components may be good, two or more sorts may be sufficient as them, and copolymerization of a part of oxy acid, such as hydroxybenzoic acid, etc. may be carried out further. As a glycol component, for example Ethylene glycol, 1,2-BUROPAN diol, 1,3-BUROPAN diol, neopentyl glycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1, 2-cyclohexane dimethanol, 1,3-cyclohexane dimethanol, 1,4-cyclohexane dimethanol, a diethylene glycol, triethylene glycol, polyalkylene glycol, 2,2-bis(beta-hydroxyethoxyphenyl)BUROPAN, etc. can be mentioned. Only one sort of these glycol components may be good, and two or more sorts may be sufficient as them.

[0012]In this invention, as a still more concrete example of polyester, Polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, The copolymer of polyhexamethylene terephthalate, ethylene terephthalate, and ethylene isophthalate, the copolymer of ethylene terephthalate and ethylene naphthalate, etc. can be mentioned.

[0013]As polyolefin resin, polypropylene, polyethylene, a polymethylpentene, polystyrene, and these mixtures and copolymer can be mentioned.

[0014]In this invention, although disperse composition of polylactic acid and the resin immiscible to this is carried out to polylactic acid, When productivity and a mechanical strength are taken into consideration, the loadings employing the feature of a whiteness degree and low density efficiently, they are 20 % of the weight of 3 % of the weight or more especially preferably still more preferably preferably 25% of the weight of 2 % of the weight or more 30 or less % of the weight more than per % of the weight. The polylactic acid film to which disperse composition of such immiscible resin was carried out forms the detailed cave which used immiscible resin as the core by carrying out biaxial extension. The feature that a whiteness degree, a mechanical strength, low density-ization, etc. increase is caused by biaxial extension being carried out.

[0015]5-1000 micrometers of thickness [8-500 micrometers of] of the film of this invention are 10-300 micrometers especially preferably still more preferably preferably. Handling nature is good if thickness is 5 micrometers - 1000 micrometers.

[0016]At least one side of the film which contains a detailed cave in this invention in the inside which makes a main constituent polylactic acid and resin immiscible to this, It is preferred to consider it as the film which laminated the layer which does not contain a cave substantially [it is desirable and / both sides] in respect of the immiscible prevention from omission of resin in a manufacturing process, surface smooth nature, easy adhesiveness, etc. As resin used for this layer that does not contain a cave substantially, the above-mentioned polylactic acid, polyester, and polyolefine can be used. Although the thickness in particular of this lamination is not limited, 1 to 30% of its total film thickness is preferred, for example, and 2 to 20% of especially its range is preferred.

[0017]In order to raise the whiteness degree of the white film of this invention further, a white pigment can also be made to contain in the layer which does not contain the film containing a cave, and/or a cave. As this white pigment, a titanium dioxide, barium sulfate, a zinc oxide, calcium carbonate, etc. can be used, for example.

[0018]Next, the manufacturing method of the white polylactic acid film of this invention is explained.

[0019]As a polymerization method of polylactic acid, it is also possible to adopt any methods, such as a condensation-polymerization method and a ring-opening-polymerization method, and a small amount of chain elongation agents, for example, a diisocyanate compound, a diepoxy compound, an acid anhydride, etc. may be further used for molecular weight increase. It is good from the practical use characteristic and molding workability that it is the range of 10,000-1 million preferably as weight average molecular weight of the polymer obtained in this way.

[0020]In this invention, there is no restriction in particular in the method of blending immiscible resin with the polylactic acid obtained above, and a publicly known mixing method is adopted as it. With for example, the Banbury mixer after adding the chip of dry immiscible resin to the chip of polylactic acid if needed and mixing with a ribbon blender, a tumbler, a Henschel mixer, etc., one axis, or a biaxial extrusion machine. It is the method of kneading and obtaining the constituent of a pellet type and which cylindrical and powdered shape at the temperature of 170-250 **. What is called a masterbatch that blended immiscible resin with high concentration beforehand at polylactic acid is made by the above-mentioned method, this and polylactic acid can be mixed, and it can also be considered as the constituent of final concentration.

[0021]Thus, there is no restriction in particular also in the method of manufacturing a film from the obtained constituent. For example, vacuum drying of said constituent is carried out at 100-140 **, it is supplied to an extrusion machine, and is heated and fused to the temperature more than the melting point. As extrusion

temperature, the range of 200-270 °C is preferred. Subsequently, the fused polymer is extruded from the T die which has a slit shape delivery, adhesion solidification is carried out at a cooling roller, and a cast film is obtained. In order to raise the adhesion of a melting sheet and a cooling roller, it is preferred to adopt electrostatic impression contact printing and oil-level spreading contact printing. When providing the layer which does not contain a cave, the method by co-extrusion can be used.

[0022]Biaxial extension of this cast film is carried out further. As this biaxial extending method, by the roll extending method, it can extend to a lengthwise direction and, subsequently to the cross direction, the serial biaxial extending method which extended by the tenter or made an order of the extension reverse, and the in-every-direction simultaneous biaxial extending method for having used the tenter can be adopted, for example.

[0023]As a temperature of this biaxial extension, the neighborhood of glass transition temperature of polymer, for example, 60-120 °C, is preferred. As draw magnification, each 2.5 to 10 times as many every direction is preferred. Once carrying out biaxial extension, it can also extend again length or horizontally further.

[0024]Thus, the obtained biaxial oriented film is heat-treated. As this heat treatment temperature, 90-160 °C is preferred and 110-140 °C is more preferred. Heat treating time is 1 second - 5 minutes preferably. The heat contraction characteristic can be adjusted with this heat treatment condition. For example, heat shrinking stress can be adjusted by providing quenching or annealing, and a intercooling zone for a film after heat treatment. In the time of heat treatment, or a subsequent annealing zone, it may loosen a lengthwise direction or crosswise.

[0025]In the film of this invention, the coating layer for improving wettability and an adhesive property can also be formed in the one side or both sides if needed. An aqueous solution and the thing emulsified or suspended are used for coating liquid in respect of explosion protection nature or environmental pollution. Although there is the method of carrying out extended after applying to the film before the method of applying to the biaxial oriented film after crystal orientation completion or crystal orientation completion, in order to make the effect of this invention reveal more notably, the latter method of a coating layer is preferred.

[0026]Especially as this method of applying, although not limited, it is preferred to apply using a roll coater, a photogravure coating machine, a reverse coating machine, a kiss coating machine, a bar coating machine, etc. Before applying, corona discharge treatment may be performed to a spreading side in air and other various atmosphere if needed.

[0027]A defoaming agent, an ultraviolet ray absorbent, a color, etc. may be further blended with the coating layer in this invention.

[Measuring method of the characteristic] The contamination of trouble occurrences, such as a film tear, or a film production device at the time of (1) film-production nature film production was judged in accordance with the following standards.

[0028]O : film production is stable and good.

[0029]**: A film tear occurs occasionally or the drum of a film production device and a roll portion become dirty. For a ***** reason, it is inferior to film production nature.

[0030]x: Film tears occur frequently and film production nature is poor.

[0031]Here, O and ** can adopt practically.

(2) The specific gravity sample was cut into the size of 50mm(TD) x60mm(MD), using high precision electronic hydrometer SD-120L (product made from Mirage Trade), with the underwater substitution method, it measured and specific gravity was computed.

(3) Whiteness degree (%)

Using spectrum type color difference meter SE-2000 (made by Nippon Denshoku Industries Co., Ltd.), tristimulus-value [of a color] X, Y, and Z were measured, and it computed from the following formula.

[0032]

The rate of whiteness degree $x[(\%) = 4]0.847xZ - 3xY$ (4) cushion (%)

Film thickness was measured having attached the standard gauge head (No.90030) to the dial gage (Mitoyo factory No.2109-10), and having applied load (50g and 500g) to the presser-foot partial upper part, and it computed from the following formula.

[0033]Rate of a cushion (%) = $\{1 - (\text{thickness at time of 500g load}) / (\text{thickness at the time of 50g load})\}$ As a rate of x100 cushion, not less than 5% is preferred.

[0034]

[Example]Hereafter, although an example explains this invention still in detail, this invention is not limited to the following example.

[0035]After carrying out the dry blend of the ethylene terephthalate ethylene isophthalate copolymer (amount % of 18 mol of isophthalic acid copolymerization) pellet 15 weight section to poly (L-lactic acid) (1.2% of mixing percentage [of D object] : glass transition temperature of 64 **) pellet 100 weight section which is the example 1 molecular weight 100,000, The biaxial extrusion machine with which hands of cut differ was supplied, and it extruded and pelletized at 220 **.

[0036]Performed vacuum drying at 120 ** for 5 hours, supplied the obtained pellet to the extrusion machine, fused it at 235 **, carried out melting extrusion from the T die at the tip of an extrusion machine at the sheet shaped, it was made to stick to a rotary cooling drum by the electrostatic impressing method, cooling solidification was carried out, and the unextended sheet was obtained.

[0037]Subsequently, subsequently the tenter was used for the longitudinal direction 3.0 times at 68 ** using the roll which heated this unextended sheet, biaxial extension was carried out crosswise one by one 3.2 times at 68 **, it heat-treated at 140 **, and the 50-micrometer-thick biaxial oriented film was obtained.

Film production is extremely stable.

It was good.

[0038]Although the characteristic of the obtained film was shown in Table 1, it had low-density-ized and excelled in a whiteness degree and cushioning properties.

[0039]The biaxial extrusion machine which adds titanium dioxide 15 weight section with a mean particle diameter of 0.3 micrometer to poly (L-lactic acid) pellet 100 weight section used in comparative example 1 Example 1 and with which hands of cut differ after mixing was supplied, and it extruded and pelletized at 220 **.

[0040]Performed vacuum drying at 120 ** for 5 hours, supplied the obtained pellet to the extrusion machine, fused it at 235 **, carried out melting extrusion from the T die at the tip of an extrusion machine at the sheet shaped, it was made to stick to a rotary cooling drum by the electrostatic impressing method, cooling solidification was carried out, and the unextended sheet was obtained.

[0041]Subsequently, although the tenter was subsequently used for the longitudinal direction 3.0 times at 68 ° using the roll which heated this unextended sheet and it tried crosswise to carry out biaxial extension one by one 3.2 times at 68 °, tears occurred frequently and film production nature was poor.

[0042]Although the characteristic of the film extracted in part was shown in Table 1, low-density-izing was insufficient.

[0043]The film was created like the comparative example 1 except having changed the loadings of the comparative example 2 titanium dioxide into five weight sections. Film production nature was °.

[0044]Although the characteristic of the obtained film was shown in Table 1, a whiteness degree and cushioning properties were insufficient.

[0045]Although film-ization was tried like the comparative example 2 except having changed the titanium dioxide with comparative example 3 mean particle diameter of 0.3 micrometer into calcium carbonate with a mean particle diameter of 1.5 micrometers, tears occurred frequently and film production nature was poor.

[0046]Although the characteristic of the film extracted in part was shown in Table 1, a whiteness degree and cushioning properties were insufficient.

[0047]The biaxial oriented film was obtained like Example 1 except having changed the kind of pellet blended with a poly (L-lactic acid) pellet, and loadings as shown in the two to example 5 table 1.

[0048]Although the characteristic of a film and the evaluation result of image quality which were obtained in Table 1 were doubled and shown, the film of the range of this invention showed the good characteristic.

[0049]After carrying out the dry blend of the ethylene terephthalate ethylene isophthalate copolymer (amount % of 18 mol of isophthalic acid copolymerization) pellet 10 weight section to poly (L-lactic acid) (3% of mixing percentage [of D object] : glass transition temperature of 63 °) pellet 100 weight section which is the example 6 molecular weight 100,000, The biaxial extrusion machine with which hands of cut differ was supplied, and it extruded and pelletized at 220 °.

[0050]Performed vacuum drying at 120 ° for 5 hours, supplied the obtained pellet to the extrusion machine, fused it at 235 °, carried out melting extrusion from the T die at the tip of an extrusion machine at the sheet shaped, it was made to stick to a rotary cooling drum by the electrostatic impressing method, cooling solidification was carried out, and the unextended sheet was obtained.

[0051]Subsequently, this unextended sheet was extended 4.0 times and crosswise at 70 ° at the longitudinal direction using the simultaneous biaxial drawing machine, it heat-treated at 140 °, and the 50-micrometer-thick biaxial oriented film was obtained. Film production is extremely stable.

It was good.

[0052]Although the characteristic of the obtained film was shown in Table 1, it has low-density-ized and excels in a whiteness degree and cushioning properties.

[0053]The co-extrusion laminating device which one set of the main extrusion machine of 71 examples and a subextrusion machine joins, provides a sublayer in both sides of a main stratum, and can create a double-sided laminated film is used, After carrying out the dry blend of the ethylene terephthalate ethylene isophthalate copolymer pellet to the main extrusion machine at the poly (L-lactic acid) pellet of Example 1, After supplying the pellet extruded and created and mixing a titanium dioxide to a subextrusion machine at the poly (L-lactic acid) pellet of the comparative example 2, the pellet extruded and created was supplied.

Each supplied pellet was supplied after carrying out vacuum drying at 120 °C beforehand for 5 hours. Two sets of extrusion machines were heated at 235 °C, melting extrusion was carried out from the T die at the tip of an extrusion machine at the sheet shaped, it was made to stick to a rotary cooling drum by the electrostatic impressing method, cooling solidification was carried out, and the thickness ratio of the sublayer / main stratum / sublayer obtained the unextended lamination layer sheet of 5/90/5.

[0054]Subsequently, subsequently the tenter was used for the longitudinal direction 3.0 times at 68 °C using the roll which heated this unextended lamination layer sheet, biaxial extension was carried out crosswise one by one 3.2 times at 68 °C, it heat-treated at 140 °C, and the 50-micrometer-thick biaxial oriented film was obtained. Film production is extremely stable.

It was good.

[0055]Although the characteristic of the obtained film was shown in Table 1, it had low-density-ized and excelled in a whiteness degree and cushioning properties.

[0056]

[Table 1]

表 1

実施例	層構成	主ポリマー	配合物	配合量	製法	製成性	比重	白度	クッション性
実施例 1	単層	ポリ(1-乳酸)	エチレンテレフタレート-エチレンイソフタレート共重合体 (イソフタル酸共重合率 1.8 モル%)	15 重量部	逐次 2 軸	○	0.63	115%	20%
実施例 2	単層	ポリ(1-乳酸)	エチレンテレフタレート-エチレンイソフタレート共重合体 (イソフタル酸共重合率 1.8 モル%)	5 重量部	逐次 2 軸	○	0.87	100%	12%
実施例 3	単層	ポリ(1-乳酸)	エチレンテレフタレート-エチレンイソフタレート共重合体 (イソフタル酸共重合率 1.8 モル%)	30 重量部	逐次 2 軸	△	0.40	120%	45%
実施例 4	単層	ポリ(1-乳酸)	ポリ(エチレンテレフタレート-エチレンイソフタレート共重合体 5 モル%)	10 重量部	逐次 2 軸	○	0.71	107%	22%
実施例 5	単層	ポリ(1-乳酸)	ポリプロピレン	10 重量部	逐次 2 軸	○	0.60	112%	24%
実施例 6	単層	ポリ(1-乳酸)	エチレンテレフタレート-エチレンイソフタレート共重合体 (イソフタル酸共重合率 1.8 モル%)	15 重量部	同時 2 軸	○	0.57	117%	27%
実施例 7	動/主層 の 3 層構造	主層 ポリ(1-乳酸)	エチレンテレフタレート-エチレンイソフタレート共重合体 (イソフタル酸共重合率 1.8 モル%)	主層 15 重量部	逐次 2 軸	○	0.68	120%	18%
比較例 1	単層	主層 ポリ(1-乳酸)	エチレンテレフタレート-エチレンイソフタレート共重合体 (イソフタル酸共重合率 1.8 モル%)	副層 5 重量部					
比較例 2	単層	ポリ(1-乳酸)	平均粒径 0.3 μm の酸化チタン	15 重量部	逐次 2 軸	×	1.30	93%	5%
比較例 3	単層	ポリ(1-乳酸)	平均粒径 0.3 μm の酸化チタン	5 重量部	逐次 2 軸	△	1.28	88%	4%
比較例 3	単層	ポリ(1-乳酸)	平均粒径 1.5 μm の酸化チタン	15 重量部	逐次 2 軸	×	1.18	105%	7%

[0057] It turns out that the thing of Examples 1-7 has the good film production nature at the time of manufacture, it low-density-izes it as compared with the thing of the comparative examples 1-3, and it excels in a whiteness degree and cushioning properties so that clearly from Table 1.

[0058]

[Effect of the Invention] According to this invention, there is no problem at the time of abandonment, it excels in white nature or cushioning properties, and the white film of low density can be provided.

[Translation done.]